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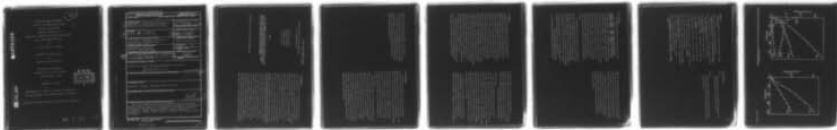
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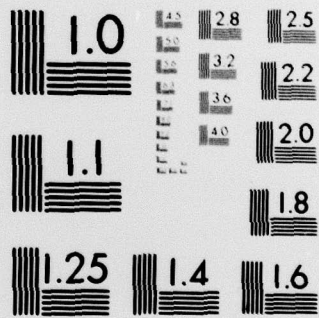
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Reactions of Water with Carbon and Ethylene
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S. Sato and J. M. White

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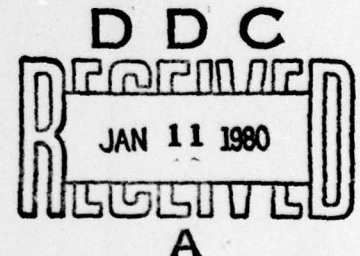
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Reactions of Water with Carbon and Ethylene
over Illuminated Pt/TiO₂. (a)

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Abstract

The room temperature reaction between gas phase water and active carbon to form carbon dioxide and hydrogen on a platinumized titanium dioxide catalyst, illuminated with band gap radiation, is reported. Using the same catalyst system, ethylene is converted to ethane, carbon dioxide, hydrogen and a small amount of methane.

(a) Supported in part by the Office of Naval Research.

1. Introduction.

The conversion of radiant energy into chemical fuels is a topic of current interest and one of the interesting observations in this area is the well known photoassisted decomposition of water in photoelectrochemical (PEC) cells [1]. Photoassisted reactions have also been carried out using heterogeneous catalysts in contact with liquid [2] or gas phase [3] reactants. For example, using illuminated, platinumized TiO₂, Kresautler and Bard [4] have reported the decomposition of liquid acetic acid to methane and Bulatov and Khidkehl [5] have reported the decomposition of acidified water. In a recent very interesting paper, Kalyanasundaram and Gratzel [6] report the photoinduced cleavage of water using a colloidal suspension of RuO₂ and Pt with Ru (bpy)₃²⁺ as a sensitizer. Inoue et al. [7] report a photocatalytic reduction of CO₂ to formic acid, formaldehyde, methyl alcohol and methane in aqueous suspensions of various semiconductors. In the gas phase, Hemmlinger et al. [8] have reported a photoassisted conversion of CO₂ and H₂O to methane at the gas-solid interface using a Pt foil contacted with a SrTiO₃ crystal. Schrauzer and Guth [9] have reported the gas phase decomposition of water and the production of NH₃ from N₂ and H₂O over illuminated TiO₂ or Fe₂O₃-doped TiO₂. Van Dams and Hall [10] repeated Schrauzer and Guth's water decomposition experiment over TiO₂ and concluded that photoassisted hydrogen evolution involves mainly surface hydroxyl groups that are present before exposure to water (i.e. H₂ production is not catalytic). Recently we have examined TiO₂ and Pt/TiO₂ catalysts for the water decomposition and the water-gas shift reaction [11]. On TiO₂ our results for water decomposition

agree with those of Van Dams and Hall [10]. Interestingly, on Pt/TiO₂ the photoassisted decomposition of water and the water-gas shift reaction were shown to be catalytic at the gas-solid interface.

We report here the photoassisted heterogeneous and catalytic reactions of C₂H₄(g) and C(s) with H₂O(g) over platinumized TiO₂. Smaller work on the latter reaction has been done by Kawai and Sakata using a RuO₂/TiO₂ system [12].

II. Experimental.

TiO₂ (anatase) was obtained from MCB and was pretreated by a 6 hr exposure to flowing hydrogen at 700°C. After cooling in the hydrogen stream it was stored in a sample vial. Platinumized (2 wt. % Pt) TiO₂ was prepared by the photodecomposition of hexachloroplatinic acid [13]. The total surface area of these catalysts was about 11 m²g⁻¹. Active charcoal was obtained from U.S. Biochemical Corporation and ethylene from Matheson. Distilled H₂O, outgassed several times at dry-ice temperature, was introduced as a gas into the reaction vessel at 24 torr, the room temperature vapor pressure. In some experiments the catalyst was cooled to 0°C during H₂O admission in order to enhance the amount of water adsorbed (we define this as a "wet" catalyst).

Reactions were carried out in an evacuable, closed circulation system (180 ml volume) linked to a mass spectrometer. The reaction cell was made of quartz and, during reaction, its temperature was maintained at 23°C by a water bath. The catalyst (0.25 g) was spread uniformly on one face of the reaction cell and outgassed at 200°C for 3 hr. After introducing reactants, it was illuminated by a 200 W high-pressure mercury lamp that was filtered through a quartz cell filled with H₂SO₄ solution to remove infrared. The gas mixture was sampled at various times and, after passage through a cold trap at about -110°C to remove H₂O, was analyzed by the mass spectrometer. In the reaction involving C(s), 5 wt. % of active charcoal was physically mixed with the Pt/TiO₂ catalyst prior to introduction into the reaction vessel.

III. Results.

Our previous experiments [11] have shown that under UV illumination Pt of Pt/TiO₂ works as a cathode and TiO₂ as a photoanode, as in PEC cells. It is therefore possible that both cathodic and anodic reactions take place simultaneously over Pt/TiO₂. This was demonstrated by the reaction of C₂H₄ with H₂O over UV-illuminated Pt/TiO₂. Figure 1 shows that C₂H₄ is rapidly converted to C₂H₆ with concomitant formation of H₂, CO₂ and a small amount of CH₄. Both H₂ and CO₂ clearly arise from the oxidation of C₂H₄ by H₂O. The CH₄ formation may be explained by the cracking of C₂H₄ during the oxidation and subsequent hydrogenation. If C₂H₄ alone is exposed to the Pt/TiO₂ a trace of C₂H₆ is formed at 23°C (self-hydrogenation). Otherwise no reaction products are found. Subsequent illumination of this mixture gives no further reaction. After C₂H₄ is consumed, C₂H₆ is then slowly oxidized despite the fact that C₂H₆ is only weakly adsorbed, indicating a fairly strong oxidative force in this system. Acetaldehyde was not detected in the products although it has been found as a partial oxidation product in the photo-oxidation of C₂H₆ on TiO₂ [14]. The product distribution in Fig. 1 does not exactly satisfy a mass balance of carbon atoms probably because of carbon deposition on the catalyst surface at the beginning of reaction.

It should be noted that the initial decomposition rate of H₂O (1 x 10⁻² torr min.⁻¹), estimated from the H₂ and C₂H₆ formation rates, is larger than the rate of water-gas shift reaction

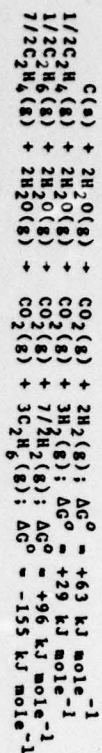
(3 x 10⁻³ torr min.⁻¹) carried out on the same catalyst [11].

This result is similar to a current-doubling effect found in PEC cells [15] but the observed difference would also occur if CO poisoned the catalyst in the water-gas shift reaction. In any case the fast initial rate suggests that the H₂ formation would become even faster by choosing a material which is more easily oxidized than C₂H₄.

Figure 2 shows the time dependence of the growth of H₂ and CO₂ for the reaction of active charcoal with gas phase water (21 torr). The initial rate of H₂ production is 1 x 10⁻² torr min.⁻¹ and tends to drop slowly as the reaction proceeds. For example, at 120 min. the rate has dropped to 0.7 x 10⁻² torr min.⁻¹. The H₂/CO₂ ratio is about 2 as expected for the reaction C(s) + 2H₂O(g) → 2H₂(g) + O₂(g). A small amount of CH₄, 0.01 torr, accumulates during the experiment. When the experiment is repeated by evacuating at 25°C and replenishing the water, the activity continues to decline slowly and, after an additional 120 min., the rate of H₂ production is 5.5 x 10⁻³ torr min.⁻¹. In the absence of C(s), small amounts of H₂(g) (0.06 torr), CO₂ and CH₄ are produced over a 2 hr. period.

Interestingly, when the catalyst was "wet" as described in the experimental section, the rate of H₂ and CO₂ evolution were drastically lowered and a stationary state was reached after 80 minutes at an H₂ pressure of 0.25 torr. In addition, a small amount of O₂ was produced. The H₂/CO₂ ratio was 1.8 and H₂/O₂ was 4.

The experiments described above indicate that the reactions



can be photoassisted at 23°C. The mechanism of photolysis of H_2O over Pt/TiO₂ may be analogous to processes occurring in PEC cells or on Schottky-type photochemical diodes [16]. Taking this view,

photon adsorption in TiO₂ forms electron-hole pairs, the hole moving to the surface and the electron migrating through the bulk of the TiO₂ eventually arriving at a Pt particle. The hole serves to oxidize some species. If water is oxidized to form an adsorbed oxygen and two protons, i.e. $O(a) + 2H^+$, the latter may migrate on the surface to a Pt particle where they can be reduced to adsorbed hydrogen atoms. Recombination of hydrogen atoms then leads to $H_2(g)$ evolution unless they react with some species such as C_2H_4 .

The mechanism and the sites involved in carbon oxidation are not clear. One possible mechanism assumes that the active charcoal interacts fairly strongly with water and the photoproducted holes are filled by an electron derived from a carbon-water intermediate and adsorbed oxygen is reduced to O^- just as in the photo-oxidation of CO [3]. If so, the resulting O^- may be attached to carbon, not titani, and form adsorbed CO. Since the water-gas shift reaction is known

to proceed under these conditions [11], subsequent reaction of adsorbed CO with $H_2O(g)$ will lead to $CO_2(g)$ and $H_2(g)$

Further speculation regarding the mechanism is not warranted and the discussion here is meant to be only

suggestive. The conversion of C_2H_4 to CO_2 and H_2 can be discussed in the same terms. The estimated quantum yield at the initial stage of both reactions is of the same order of magnitude as in the Pt-SrTiO₃ PEC cell at zero potential [17] (0.15). This can be improved, we believe, by modifying the light-catalyst geometry.

In summary, our results demonstrate that the endothermic reactions between C_2H_4 or active carbon and gaseous water can be photoassisted catalytically at room temperature over a platinumized titania catalyst. More detailed studies of the characteristics of Pt/TiO₂ and of the mechanisms of these reactions are underway.

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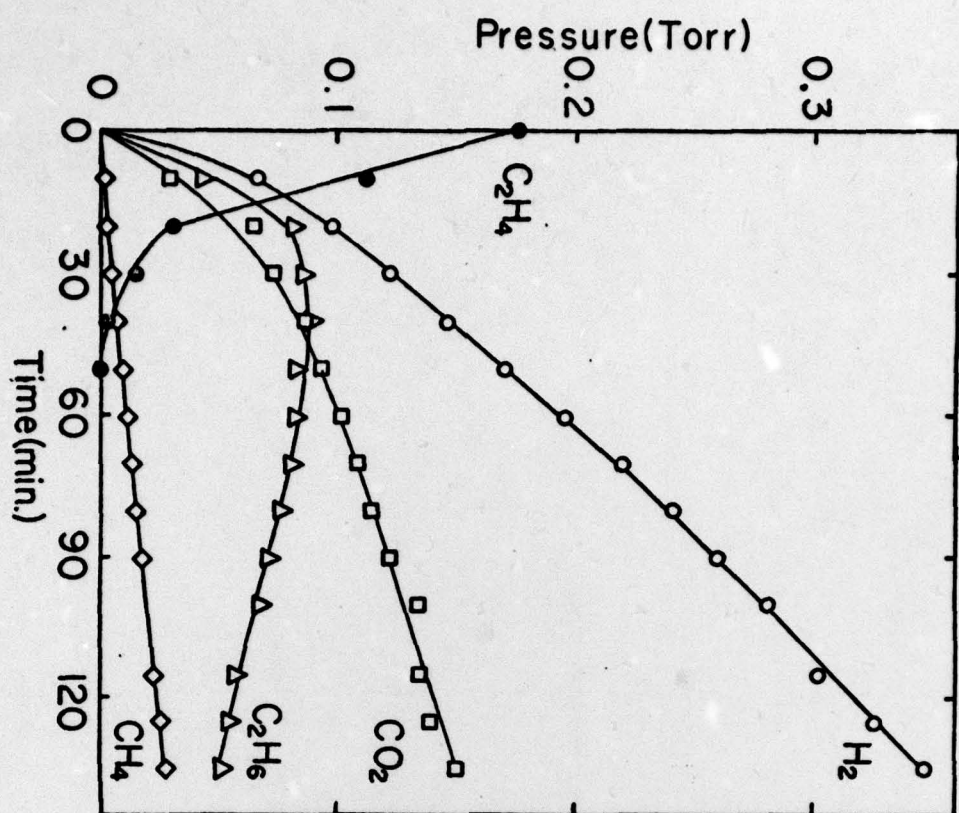
Figure Captions

Fig. 1.

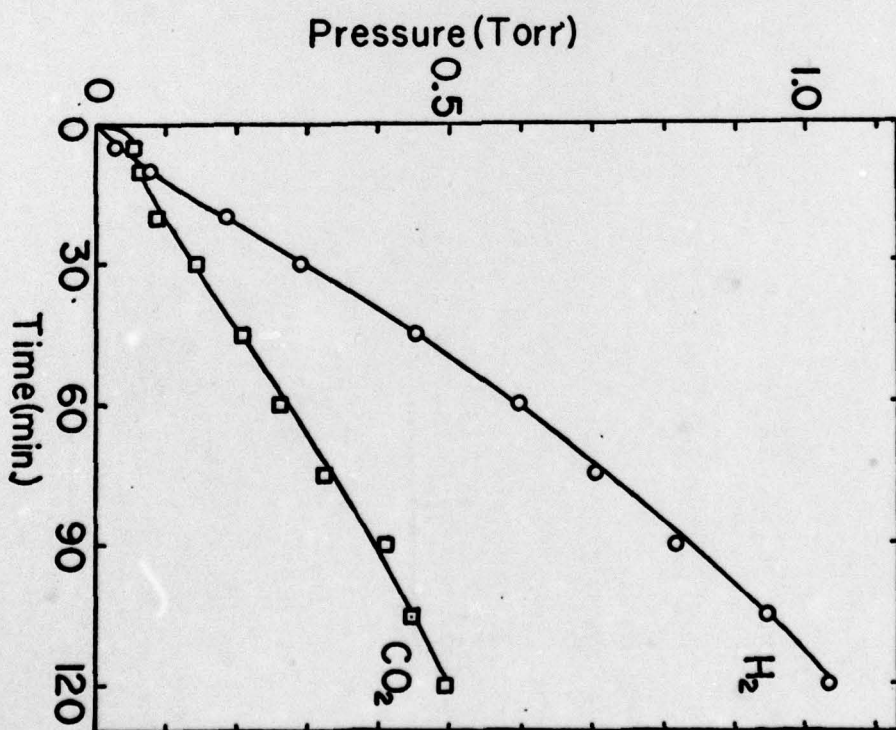
Time course of the reaction of $H_2O(g)$ with $C_2H_4(g)$ over UV-illuminated Pt/TiO₂. Pressure of H_2O is ~21 torr.

Fig. 2.

Evolution of H_2 and CO_2 during the reaction of $H_2O(g)$ with active charcoal on Pt/TiO₂ under UV illumination. Pressure of H_2O is ~21 torr.



Sato and White, Fig. 1



Sato and White, Fig. 2